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TITLE: **A METHOD OF DEPOSITING AN ELECTROCATALYST
AND ELECTRODES FORMED BY SUCH METHOD**

This application is a 371 of PCT/US98/18938, filed 9/11/1998, which claims priority from USSN

Field of the Invention   08/927,739, filed 9/11/1997, now US 6,159,533,

5   The application provides a process for depositing a minimal load of an

electrocatalyst (preferably comprising platinum) onto a support, preferably a support

capable of use as a fuel cell electrode (most preferably carbon cloth), while maximizing

the catalytic activity of the catalyst. The application also is directed to products

comprising novel electrocatalytic coatings comprising rod-shaped structures.

10   **Background of the Invention**

A fuel cell is an electrochemical device in which electrical energy is generated

by chemical reaction without altering the basic components of the fuel cell--that is, the

electrodes and the electrolyte. Fuel cells combine hydrogen and oxygen without

combustion to form water and to produce direct current electric power. The process

15   can be described as electrolysis in reverse. The fuel cell is unique in that it converts

chemical energy continuously into electrical energy without an intermediate conversion

to heat energy.

Fuel cells have been pursued as a source of power for transportation because of

their high energy efficiency (unmatched by heat engine cycles), their potential for fuel

20   flexibility, and their extremely low emissions. Fuel cells have potential for stationary

and vehicular power applications; however, the commercial viability of fuel cells for

power generation in stationary and transportation applications depends upon solving a

number of manufacturing, cost, and durability problems.

One of the most important problems is the cost of the proton exchange catalyst

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for the fuel cell. Some of the most efficient catalysts for low temperature fuel cells are

noble metals, such as platinum, which are very expensive. Some have estimated that

the total cost of such catalysts is approximately 80% of the total cost of manufacturing

a low-temperature fuel cell.

5   In a typical process, an amount of a desired noble metal catalyst of from about

$0.5-4$ mg/cm^2 is applied to a fuel cell electrode in the form of an ink, or using complex

chemical procedures. Unfortunately, such methods require the application of a

relatively large load of noble metal catalyst in order to produce a fuel cell electrode

with the desired level of electrocatalytic activity, particularly for low temperature

10   applications. The expense of such catalysts makes it imperative to reduce the amount,

or loading, of catalyst required for the fuel cell. This requires an efficient method for

applying the catalyst.

            In recent years, a number of deposition methods, including rolling/spraying,

solution casting/hot pressing, and electrochemical catalyzation, have been developed

15   for the production of Pt catalyst layers for proton exchange membrane (PEM) fuel

cells. Although thin sputtered Pt coatings deposited on carbon cloth can measurably

improve fuel cell performance, this approach generally is not considered to be viable

for large area deposition or as a stand alone treatment for applying platinum.

Continuing challenges remain in the development of scalable methods for the

20   production of large-area (>300 cm^2), high performance (>1 A/cm^2 at 0.6 V) fuel cell

electrodes with low Pt loadings (<0.3 mg/cm^2).

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Summary of the Invention

The present invention provides a method for depositing onto a support a vaporizable composition comprising a catalytic component. The method comprises converting the vaporizable composition into a vapor, and depositing the vapor onto the

5   support in an amount sufficient to produce a concentration of the catalytic component adapted to produce a catalytically effective coating on the support. The invention also is directed to electrodes produced by the method, and to electrodes comprising a support comprising a deposit disposed thereon which comprises a catalytically effective load of an electrocatalyst comprising an electrocatalytic active area at least in

10   part comprising rod-shaped structures.

Brief Description of the Figures

Figure 1 is a graph depicting the polarization performance of an experimental electrode used as cathode and anode at a cell pressure of 206.85 kPa (30 psig). The experimental electrode was made from a carbon-only ELAT carbon cloth electrode,

15   available from E-TEK, Natick, MA, bearing Pt deposited using electron beam physical vapor deposition (EB-PVD) according to the present invention, as described in Examples III and IV.

Figure 2 is a graph depicting the polarization performance at 206.85 kPa (30 psig) cell pressure of a conventional sputtered Pt catalyzed ELAT gas diffusion media

20   experimental electrode used as cathode and anode, as described in Example IV.

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Figure 3 is a graph depicting the polarization performance at 206.85 kPa (30 psig) cell pressure of a conventional sputtered Pt catalyzed ELAT gas diffusion media experimental electrode used as an anode, as described in Example IV.

Figure 4 is a graph depicting a side-by-side comparison of performance at cell
5   and compensated potentials of a conventional sputtered Pt catalyzed experimental electrode and an inventive EB-PVD Pt catalyzed experimental electrode used as a cathode showing the polarization performance at 206.85 kPa (30 psig) cell pressure, as described in Example IV.

Figure 5 is a graph depicting a side-by-side comparison of performance
10   between a conventional sputter deposited Pt electrode and an inventive EB-PVD Pt deposited electrode used as an anode showing the polarization performance at 206.85 kPa (30 psig) cell pressure, as described in Example IV.

Figure 6 is a graph depicting a side-by-side comparison of performance at cell and compensated potentials of another conventional sputter deposited Pt electrode and
15   another inventive EB-PVD Pt deposited electrode used as a cathode showing the polarization performance at 206.85 kPa (30 psig) cell pressure, as described in Example IV.

Figures 7-9 are field-emission scanning electron microscopy pictures (micrographs or FE-SEMs) of an uncatalyzed ELAT gas diffusion media at various
20   magnifications.

Figures 10-20 are FE-SEMs of ELAT gas diffusion media catalyzed using EB-PVD of Pt according to the present invention, as described in Examples III and IV, at various magnifications.

Figures 21-26 are FE-SEMs of ELAT gas diffusion media catalyzed using conventional sputter deposition of Pt, as described in Examples III and IV, at various magnifications.

Brief Description of the Invention

Vacuum deposition techniques are routinely employed in a variety of applications ranging from metallized layers in the fabrication of semiconductors to barrier coatings for food packaging, hard coatings for cutting tools, and optical thin films. Some of the typical methods employed include chemical vapor deposition, physical vapor or thermal deposition, ion sputtering, and ion beam assisted deposition (IBAD). Because the materials are deposited in a vacuum (typically less than 13.3 mPa, or 1×10^{-4} torr), contamination of the films can be minimized while maintaining good control over film thickness and uniformity. Such techniques, in many cases, lend themselves to deposition of materials over large areas via a reel-to-reel or web coating processes.

The present invention uses vacuum deposition techniques, preferably EB-PVD, to deposit a catalyst onto a support. The support for the claimed coating may be any number of materials, preferred materials being suitable for use in electrodes in fuel cells. Such materials include, but are not necessarily limited to proton exchange

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membranes (PEMs), carbon cloth, and carbon paper. Preferred supports are carbon

supports.

Suitable PEMs include, but are not necessarily limited to polymer electrolyte

membranes or ionomers, such as NAFION™, available from Dupont, Inc.,

5   Wilmington, Delaware, and most preferably a fluoroionomeric membrane comprising a

composite of polytetrafluoroethylene with impregnated ion exchange media known as

GORE-SELECT*, available from W. L. Gore & Associates, Elkton, Maryland.

Suitable carbon supports include, but are not necessarily limited to, graphite,

carbon fiber, and carbon cloth. Suitable commercially available carbon gas diffusion

10   media for use as a support include, but are not necessarily limited to: carbon gas

diffusion electrodes; iso-molded graphite; carbon bundles, preferably having 6,000 or

12,000 carbon filaments/bundle; reticulated carbon; carbon cloth; and, carbon paper.

A preferred carbon support is carbon cloth, preferably a carbon-only ELAT carbon

cloth electrode, available from E-TEK, Natick, MA.

15   The support preferably should resist corrosion in an acid environment, offer

good electrical conductivity and, for carbon supports, allow fast permeation of oxygen

(cathode) and hydrogen (anode), comply with thin layer manufacturing techniques, and

contribute little to the weight and cost of the fuel cell assembly.

A catalyst is deposited onto the support, preferably using vacuum deposition

20   techniques. As used herein, the term "catalyst" is defined as a substance that increases

the rate of approach to equilibrium of a chemical reaction without being substantially

consumed in the reaction. A catalyst works by forming chemical bonds to one or more

reactants and thereby facilitating their conversion. A catalyst does not affect the

reaction equilibrium. A catalyst provides for alternate reaction pathways/mechanisms

that offer an overall lower activation energy for the reaction, thus accelerating the rate

5   of turnover.

In electrochemical systems the reaction rate (power density/current density) is

controlled by controlling temperature and electrocatalysis. Electrocatalysts are

substances (metals, metal oxides, non-metals, organometallics, etc.) that can promote

the rate of electrochemical reactions, i.e., ionization, deionization, for a given surface

10   area. The electrocatalyst is a substance that accelerates the rate of forward and

backward charge transfer reactions for a given redox system (charge transfer reaction)

without perturbing chemical equilibrium (thermodynamics is not affected by the

presence of a catalyst). An electrocatalyst provides for alternative reaction

pathways/mechanisms that offer an overall lower activation energy for the

15   electrochemical reaction, thus accelerating the rate of electrochemical turnover. The

rate at which a reaction at an electrode surface proceeds may be limited by the intrinsic

kinetics of the heterogeneous process. In non- electrochemical systems, the

macroscopically observed reaction rate is the result of a series of elementary processes.

A key difference between an electrocatalyst and other types of catalysts is the

20   ability of the electrocatalyst to manipulate an additional driving force variable: the

electric potential. A change in potential of one volt at the surface of the

electrocatalyst/electrode can cause a change in reaction rate of eight orders of

magnitude. This change may be equivalent to an increase in temperature of several

hundred degrees Celsius for a typical catalytic reaction. (i.e., non-electrochemical

reaction). For fuel cell applications heterogeneous electrocatalysts exist as foils,

deposited films, individual particles or supported particles. The word "heterogeneous"

5   means that the reactant is normally in a different phase (gas or liquid) than the

electrocatalyst (solid).

To describe how a particular surface electrocatalyzes/catalyzes a particular

reaction requires a knowledge of three factors: the mechanism of the reaction

pathway; the chemisorption energy of the surface species; and, the effective activation

10   energy (energies) of the reaction. Metals with empty "d" orbitals are suitable

electrocatalysts because they adsorb H_2 rapidly, with low activation energies of

adsorption. Referring to the Periodic Table of the Elements, suitable electrocatalysts

include, but are not necessarily limited to: Group IVA metals (Ti, Zr, Hf); Group VA

metals (V, Nb, Ta); Group VIA metals (Cr, Mo, W); and, Group VIIA metals (Mn,

15   Tc, Re). These metals appear to adsorb H_2 with high enthalpy of adsorption.

Preferred electrocatalysts are metals which adsorb H_2 with lower heats, including but

not necessarily limited to Groups VIIIA, B, and C (Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt),

preferably Ni, Pd, or Pt, most preferably Pt. The group IB metals (Cu, Ag, Au) have

low heats of adsorption, but are not preferred as H_2 adsorption catalysts because they

20   have slow activated chemisorption.

The Group VIII metals, preferred electrocatalysts for use in fuel cell electrodes,

are believed to have heats of adsorption in a range which enables the reactant to

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chemisorb strongly enough to allow for surface reaction (electrochemical

oxidation/reduction by breakdown and discharge of adsorbed species) but not strongly

enough to form surface-bonded species. Due to the greater activation energy of

chemisorption for oxygen, electrocatalytic reactions which involve surface oxygen

5   require higher temperatures in order to produce satisfactory reaction rates than do

reactions which involve surface hydrogen. For example, the most widely used oxygen

electrodes for low temperatures are silver and platinum. Summarizing, suitable

catalysts for electrochemical applications include, but are not necessarily limited to Pt,

Pd, Ru, Rh, Ir, Ag, Au, Os, Re, Cu, Ni, Fe, Cr, Mo, Co, W, Mn, Al, Zn, Sn, with

10   preferred catalysts being Ni, Pd, Pt, most preferably Pt.

In order to apply an electrocatalytic coating to the support, the electrocatalyst

is heated to vaporization. The heating may be provided using any suitable source,

including but not limited to an electron beam, electrical resistance heating, microwave,

and laser. In a preferred embodiment, the catalyst is heated using an electron beam.

15   In a preferred embodiment, the support is placed in a vacuum chamber

provided with a crucible, preferably made of graphite, with a mechanism for directing a

high power electron beam onto a solid chunk of the catalyst to produce a catalyst

vapor. Where platinum is the catalyst, the catalyst is heated with the electron beam to

between about 2300°C-2600°C (4172°F - 4712°F) to form a vapor.

20   During the deposition process, the pressure in the vacuum chamber should be

pumped down to a pressure sufficient to cause the vapor to condense onto the support.

10

A preferred pressure is about 13.3 mPa (about 10^{-4} torr) or less. As used herein, the

term "in a vacuum" is defined to mean a pressure of about 13.3 mPa (10^{-4} torr) or less.

The vaporized catalyst preferably should be allowed to deposit or condense onto the

support in a vacuum. The temperature in the vacuum may vary; however, the

5   temperature should be low enough not to damage the support, and low.enough to

permit the catalyst vapor to condense onto the support. Preferably, the temperature

should be about 100-200°C or less. The deposition rate preferably should range from

about 0.5-10Å/sec.

The deposition should continue until a catalytically effective amount of the

10   catalyst is deposited onto the support. As used herein, the term "catalytically

effective" is defined to mean effective to catalyze the necessary reactions. The term

"catalytically effective amount" is defined to mean as small an amount of the catalyst as

possible to result in enough active catalyst to catalyze the necessary reactions.

Typically, the amount of catalyst deposited to result in a catalytically effective amount

15   should be from about 0.01 to about 0.3 mg/cm^2, preferably less than about 0.2 mg/cm^2.

The thickness of the coating may be monitored by standard methods, e.g., using the

frequency change of a quartz crystal oscillator. The weight of the film may be

determined by weighing a known area of the support before and after depositing the

film.

20   The support preferably is used as an electrode in a fuel cell. Preferred fuel cell

electrodes are as thin as possible, typically having a thickness between about 0.010-

0.175 inches. Where the support is a PEM, the PEM preferably should be treated with

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a carbon catalyst support, such as carbon ink, using standard techniques well known in the art. Carbon supports preferably should be wet-proofed.

Individual membranes or electrodes may be prepared, or the process may be scaled up for production purposes. Where the support is thermally sensitive, cooling

5   may be required. In the laboratory, cooling may be accomplished by mounting the support on the surface of an aluminum cylinder which is rotated through the ion and coating flux. With this setup, water cooling is no longer necessary because of the sufficiently large thermal mass of the cylinder combined with the fact that the support is no longer continuously exposed to the ion beam and coating flux. This fixture

10   appears to hold promise from a scale-up perspective as large areas of support material can be rolled up on a drum and coated in a reel-to-reel process. Preferably, a scaled up arrangement will be a reel-to-reel arrangement in vaccuo. The coating technique described herein is adaptable for use with conventional "web coating" technologies.

Upon incorporation into a membrane electrode assembly and into a fuel cell

15   supplied with hydrogen gas under suitable flow conditions, the electrocatalytic coating of the invention exhibits an open circuit voltage of at least about 0.8V, preferably about 1V. The term "open circuit voltage" or "open cell voltage" is defined as the spontaneous potential or voltage present in a fuel cell when no current is allowed to flow. This potential is known as the cell equilibrium potential and its theoretical value

20   can be derived from thermodynamics using the Nernst relationship:

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$$E = E^{o} + \frac{RT}{nF}\ln\left[\frac{\prod(\text{reactant activity})}{\prod(\text{product activity})}\right] \qquad [1]$$

where n is the number of electrons participating in the reaction, F is the Faraday's

constant (96,439 coulombs/g-mole electron), R is the universal gas constant, T is the

cell temperature and E^{o} is the reversible standard cell potential for the reaction, which

5   is directly related to the maximum electrical work W_e obtainable in a fuel cell operating

at constant temperature and pressure and is thermodynamically given by the change in

Gibbs free energy (ΔG) of the electrochemical reaction:

$$W_e = \Delta G^{o} = -nFE^{o} \qquad [2]$$

For the overall cell reaction, the open circuit potential increases with an

10 increase in the activity of reactants and a decrease in the activity of products. Changes

in cell temperature and pressure also influence the reversible cell potential. Practically,

the open circuit voltage is the maximum voltage attainable during a fuel cell

polarization or I V curve, and corresponds to the cell potential at which the drawn net

cell current is zero.

15 For example, after appropriate equilibration time, a PEM fuel cell will observe

an open circuit voltage of from about 0.8 V and about 1 V versus a reference standard

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hydrogen electrode when operating: (a) at a temperature of from about 50° C to about 130° C; (b) with hydrogen and air as reactants; (c) humidified at a temperature of from about 50° C to about 140° C; (d) with relative humidities of from about 0 to about 100 %; (e) with pressures of from about 0 to about 100 psig; and, (f) with flows

5   large enough to assure complete irrigation of the electrocatalyst phase throughout the electrode.

The vacuum deposition techniques of the present invention are capable of forming large-area (>300 cm^2), high performance fuel cell electrodes with low Pt loadings (<0.3 mg/cm^2, preferably about 0.1 mg/cm^2) which are capable at a cell

10   potential of about 0.6V of producing a power output of well over 400 mA cm^{-2}, preferably over about 800 mA cm^{-2}, most preferably about 1000 mA cm^{-2}, under the following conditions: in a single cell fuel cell fixture; with appropriate gas distribution manifolds and appropriate gasketing; using ELAT as gas diffusion material; with appropriate cell compression (from about 5.65 to about 33.89 N m/bolt, or about 50 to

15   about 300 lb in/bolt compression torque); at cell operating conditions which typically include water saturation of the anode and (H$_2$) reactant feed at humidification temperatures of from about 40 to about 90°C; cell temperatures of about 40 to about 80°C; volumetric flowrate reactant feeds of about 1.2 -2 and about 2-5 times the stoichiometric value, for H$_2$ and air, respectively; and cell pressure set from about 0 to

20   about 413.7 kPa gauge (1 and about 60 psig) for the anode (H$_2$ electrode) and cathode (air electrode).

Tafel analysis on experimental cathodes (described in Example IV)

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demonstrates about a five-fold difference in oxygen reduction exchange current density

between the vapor deposition techniques of the present invention and conventional

sputtered electrodes ($i_{o,PVD}/i_{o,sput} \sim 4.89$). The difference suggests that vapor deposited

cathodes, such as the EB-PVD Pt deposited cathodes formed in Examples III and IV,

5   have a substantially larger electrocatalytic active area or "three phase boundary"

(TPB) than conventional sputtered Pt cathodes. This electrochemical conclusion was

confirmed by field-emission scanning electron microscopy pictures (micrographs or

FE-SEMs). FE-SEMs showed the presence of a microstructure in the inventive vapor

deposited electrodes with readily recognizable Pt particles and the presence of "rod-

10   shaped" structures 10, which become visible beginning at about x10k magnification, as

shown in Figs. 14-15 and 17-22. These rod-shaped particles were not observed in the

sputtered sample, as shown in Figs. 23-28.

For purposes of the present application, the term "rod-shaped" is defined to

mean substantially cylindrical shaped structures having a diameter 10a, as shown in

15   Fig. 17, and a length 10b, as shown in Fig. 17. The rod-shaped structures shown in

Figs. 12-13 and 15-20 have (a) a diameter 10a (Fig. 17) of from about 40-about 60

nm, typically about 60 nm, and (b) a length which is difficult to verify, but appears to

vary.

Electrodes made according to the present invention may be used in fuel cells

20   having many different constructions known to those skilled in the art. The invention

will be better understood with reference to the following examples, which are for

illustrative purposes only and should not be construed as limiting the invention, which

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is defined by the claims.

EXAMPLE I

Using a vacuum chamber 2 m long and 1.5 m in diameter, candidate coatings were first deposited on glass slides and small coupons of representative membrane and

5   electrode material, and subjected to compositional and microstructural analysis. Next, a series of larger-area electrode materials were coated and evaluated using a small home-built test cell, described below.

After a final down-selection, a limited number of full scale 150 cm^2 electrodes were fabricated and tested. Special sample fixtures, described in more detail in

10   Example II, were developed to allow for the coating of carbon cloth electrodes over areas as large as 300 cm^2. Samples up to 250 cm^2 were coated using a planetary gear arrangement. The samples were asynchronously rotated through an electron beam- physical vapor deposition (EB-PVD) coating flux to ensure uniform deposition of the Pt over the entire electrode surface.

15   Carbon cloth and carbon paper materials, both plain and wet-proofed (i.e. coated with TEFLON$^®$), were coated with 0.01, 0.05, and 0.10 mg/cm^2 of Pt. In addition, wet-proofed samples treated with a layer of carbon-only ELAT were procured from E-TEK for Pt coating in a similar manner.

A comparison of the thicknesses, morphologies, and Pt distributions of selected

20   fuel cell electrode materials was performed using scanning electron microscopy (SEM)

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and transmission electron microscopy. The objective of such measurements was to determine the effect of electrode structure on the resulting efficiency of the fuel cell.

Performance analysis of catalyst coated electrode materials was undertaken using a small "home-built" test cell. The simple test cell consisted of two 6.9 cm

5 stainless steel flanges used as collector plates with single air/hydrogen inlets and pairs of 100-mesh stainless steel screens mounted on each side of the electrode to provide a degree of gas diffusion. The cell active area was approximately 64 cm^2 and the same electrode material was used for both the anode and the cathode. The system was pressurized with humidified hydrogen and compressed air at 96.53 kPa (14 psig) and a

10 flow rate of ~0.5 liters per minute. Current-voltage tests were conducted at ambient temperature at each outlet.

In all tests, the EB-PVD Pt-coated ELAT material repeatedly demonstrated superior behavior compared to a higher loaded control material, namely E-TEK platinum over VULCAN XC-72 ELAT solid polymer electrolyte electrode (4 mg/cm^2).

15 Measurable improvements in efficiency were observed for the carbon cloth with increasing Pt loading. It was also possible to further reduce the Pt loading of the EB-PVD coated carbon-only material on the anode side to as low as 0.01 mg/cm^2 with minimal reduction in performance.

EXAMPLE II

20 Fabrication and testing of three full scale 150 cm^2 electrodes was performed based on the results of the screening tests with the small test fixture.
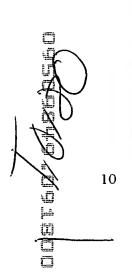
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The electrodes prepared for testing are summarized in Table 2.

TABLE 2

Sample I.D.	Membrane/Electrode Material	Deposition Method	Pt Loading (mg/cm²) (Anode/Cathode)
1	20 μm GORE SELECT®/C-only ELAT	EB-PVD Pt	0.10/0.01
2	50 μm GORE SELECT®/C-only ELAT	EB-PVD Pt	0.05/0.05
3	20 μm GORE SELECT®/C paper	Sputtered Pt	0.10/0.10

In order to effectively evaluate the full-scale electrodes, a Scribner Associates

Model 890 load system was leased for use with a test fixture. Basically, the test fixture

consisted of the chosen membrane sandwiched by the chosen electrodes surrounded

by graphite plates having flow channels to allow the passage of hydrogen and oxygen

gas into contact with the electrodes. A metal plate sandwiched the assembly on each

side. The metal plates had suitable holes drilled for introducing the hydrogen and

oxygen gas, and electrical leads collected current and connected each plate to the load

unit. The 1 kW, 125 amp Scribner load unit recorded all performance data from the

cell while controlling the temperatures of the cell and feed gases, ensuring consistent,

repeatable results. The comparison test fixture was rated at more than 100 watts

depending on the configuration and operational mode. The modular design of the cell allowed for many different possible configurations and use of different material thicknesses.

Particular attention was paid to the gas handling system in assembling the test

5   cell. All of the tubing and connectors were made of a 316 stainless steel and TEFLON (where electrical isolation was needed) in an effort to limit transport of metal cations into the cell. The gases were passed through a pair of Perma Pure Inc. NAFION-based humidifiers and then carried to the cell via stainless tubing wrapped in heater tape to maintain proper temperature. Next, each gas was directed into 3-branch

10 manifolds for the gas inlets and outlet. Exhaust gases were passed through a pair of flowmeters to measure the amount of excess fuel and air flow. Flowmeters were not installed on the upstream side as they contain a significant amount of aluminum parts which may contaminate the gases and hinder cell performance. A stainless steel reservoir with a built in heater was used to heat the cell and was controled by the

15 Scribner load unit. A plastic submersible chemical pump circulated deionized water in a closed circuit composed of TEFLON tubing through the cell and humidifiers and back to the container. No active cooling of the cell was needed.

Performance tests typically were conducted at a temperature of 60°C, 30 psi humidified gasses, 3.5 time Stoichiometric Ratio (SR) or less on the air side, and 2 SR

20 or less on the reactant side. The first objective was to match the performance curves for the electrode of the present invention with the control, comprising an electrode from a Gore PRIMEA® membrane electrode assembly, available commercially from

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W.L. Gore & Associates, Inc., under similar test conditions. After assembly, the cell

was conditioned for several hours at low current. Once the performance stabilized,

current voltage data was acquired starting at high currents and slowly ramping down.

Once the performance curve of the test membrane/electrode assembly had been

5   matched with the performance curves of the controls, testing was performed. The cell

was first conditioned for eight hours at a low current setting with humidified gasses at

30 psi. The highest current density achieved using the 100nm/10nm EB-PVD Pt-

coated ELAT with the 20 μm membrane was 732 mA/cm^2 at .358 V. In general, the

overall power output of EB-PVD deposited electrode was 10-50% less than the output

10   of the control. However, it is important to point out that this performance was

achieved with less than 20% of the total Pt loading of the baseline material.

The foregoing tests demonstrate successful use of EB-PVD in the fabrication

of 150 cm^2 membrane electrode assemblies with total Pt loadings as low as 0.11

mg/cm^2.

15   **EXAMPLE III**

Experiments were performed to characterize the electrochemical (fuel cell

performance) and morphological properties of experimental electrodes prepared by Pt

EV-PVD and magnetron sputtering of ELAT® gas diffusion media. MEAs prepared

with PVD electrodes (cathodes or anodes) yielded superior polarization performance

20   compared to the sputtered half cells.

20

Electrode preparation: Vacuum vaporization-based catalyzed electrodes were

prepared using (a) electron-beam physical vapor deposition (EB-PVD) according to

the present invention, and (b) conventional magnetron sputtering of Pt. In each case,

the Pt was deposited onto double-sided ELAT commercial carbon-cloth gas diffusion

5   media. The catalyzation took place onto the "active side" of the diffusor, i.e., on the

side normally in contact with electrocatalyst layers.

For EV-PVD, a catalyst deposition rate of 1 Å/sec was chosen. The chamber

base pressure was about 13.3 mPa (10^{-5} torr). The Pt source was 99.95% purity.

For magnetron sputtering, a 15.24 cm (6 in) diameter magnetron sputtering

10   unit was used to sputter Pt onto the substrate at a rate of about 2 to about 3 Å/sec.

The chamber base pressure was about 1.33 mPa (10^{-4} torr). The Pt target was a foil

with a purity 99.99%.

Electrodes at a loading level of 0.1 mg Pt cm^{-2} were prepared using both

techniques and compared. Energy dispersive spectroscopy (EDS) x-ray analysis

15   detected only Pt as the vaporized phase using either technique. The catalyst layers

formed using either technique had an average thickness of about 500Å.

The Pt-catalyst electrodes were incorporated into experimental MEA's using

methods known in the art. In order to solely characterize the performance of the

vacuum coated electrode, *e.g.*, as cathodes, MEA's were prepared using a Gore

20   PRIMEA® membrane electrode assembly as an anode, and vice versa when the vacuum

coated electrode was characterized as the anode half cell. The Gore PRIMEA®

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membrane electrode assembly presented a loading of 0.1 mg Pt cm^{-2} and the

experimental MEA's used a 30 μm GORE SELECT® (950EW) perfluorinated

membrane to form a membrane electrode assembly in all cases.

EXAMPLE IV

5   *Fuel Cell and Tafel Performance Tests:* To electrochemically characterize the

performance of the experimental electrodes as cathodes and anodes, H$_2$/air fuel cell

testing analysis was performed. The MEAs containing electrode active areas of 25 cm^2

and 30 μ GORE SELECT® membranes were mounted in standard fuel cell reactor

fixtures using ELAT gas diffusion media for the reference half cell and were clamped

10   to standard compression levels. The fuel cell test was conducted using a fuel cell

station commercially available from Globetech, Inc., Bryant, TX. For the pressurized

experiments, a 103.43/103.43 kPa and 206.85/206.85 kPa (15/15 psig and 30/30 psig)

gauge anode and cathode, respectively; the cell temperature was set at about 80°C

with anode and cathode feeds humidified at about 60-70°C and 85°C; and, flowrates

15   set at 2/3.5 times the stoichiometric value for H$_2$ and air, respectively. In some tests, a

constant flow of 500-1000 standard cm^3/min was used for the H$_2$ and air, respectively.

For the atmospheric pressure runs, the cell temperature and reactant humidification

was set at about 60°C. The performance was evaluated at different times on stream

(TOS).

20   *Fuel Cell Performance Analysis:* Fig. 1 shows the polarization performance at

206.85 (30 psig) cell pressure of a Pt EB-PVD catalyzed ELAT gas diffusion media

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experimental electrode used as a cathode and anode. The MEA used was a Gore PRIMEA® membrane electrode assembly (anode or cathode). Figs. 2 and 3 are the equivalent graphs (at different cell pressures) for the Pt-sputtered experimental electrode used as cathode and anode. Polarization performance from these graphs

5 suggests that the Pt evaporated electrode displayed superior performance compared to the sputtered electrode for both cathode and anode operation.

Figures 4 and 5 show a side-by-side comparison of performance between both vacuum catalyzation technologies. When used as a cathode, the inventive PVD catalyzed electrode showed improved performance throughout the entire polarization

10 curve, i.e., OCV, activation region, ohmic region and mass transport region, compared with the sputtering catalyzed electrode (Fig. 4). For example, at 0.6V, the MEA containing the PVD half cell operating as cathode yielded about 400 mA cm^{-2} with an OCV of 0.889 V against 60-100 mA cm^{-2} and OCV of 0.779-0.810 V for the sputtered system (i.e., 4 times lower performance). The compensated (IR-free) performance for

15 the sputtered system followed the curve for the total cell potential indicating that the controlling electrode was the cathode half cell.

Fig. 5 shows the same analysis, but with the vacuum vaporized electrode used as anode. Here, although the OCV and the catalyst regions of the polarization curves were comparable for both systems (as expected due to the reference cathode operating

20 as cathode in both cases), the IR region and the mass transport region for the MEA containing the sputtered electrode demonstrated substantially lower performance, i.e., larger slope, (larger membrane resistance and anode linear polarization losses) and

23

more pronounced mass transport effects. For example, at 0.6 V cell potential, the

MEA containing the sputtered anode yielded between 300 and 400 mA cm^{-2} while the

PVD anode-containing MEA yielded almost 1000 mA cm^{-2}. The difference in

performance observed in this case (experimental electrode used as anode) was mostly

5   due to anode polarization differences: at 0.6 V the sputtered anode suffered about 240

mV polarization loss against 92 mV polarization loss for the EB-PVD cathode.

Tafel Analysis: In order to rationalize the difference in performance of

electrodes made using EB-PVD versus sputtering, the electrocatalytic

activity/activation polarization performance of the electrode was probed using a Tafel

10   analysis. Briefly, a fuel cell polarization curve can be described using the semi-

empirical equation:

$$E = E_o - b\log i - iR - me^{ni}$$

where the first negative term ($-b\log i$) indicates the cathode activation loss

(electrocatalyst/electrodics, i.e., resistance to charge transfer), the second negative

15   term ($-iR$) addresses the ohmic losses due to membrane resistance, contact potential

and anode linear polarization losses, and the third negative term ($-me^{ni}$) addresses mass

transport polarization losses. During a Tafel analysis, the ohmic and mass transport

losses are normally eliminated and electrocatalytic parameters are measured by curve

fitting the data to the following expression:

20       $$E_c = E + iR \simeq E_o - b\log i$$

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where the compensated (iR-free) cell potential is used to eliminate any ohmic loss that could be present in the catalyst region of the polarization curve. The Tafel slope, b and the parameter E_o (which is related to the exchange current density i_o, and, thus related to the polarizability of the interface due to its dependence with the intrinsic

5   electrocatalytic activity and the length of three phase boundary, TPB, i.e., number of electrocatalytic active sites or electrochemically active surface area) were then evaluated for the evaporated and sputtered vacuum coated electrodes used as a cathode (controlling half cell). The experimental Tafel curve is shown in Fig. 6.

Tafel analysis suggested that, although the Tafel slope for the evaporated

10   electrode was larger than the sputtered electrode, the PVD cathode provided a substantially larger electrocatalytic active area (larger TPB) than the sputtered cathode, as found comparing the E_n values for both electrodes 1.145V (PVD) versus 0.853 V (sputtering). The superior polarization performance of the PVD electrode compared with the sputtered electrode can then be explained on the basis that the exchange

15   current density i_o for oxygen reduction in the evaporated electrodes was about 5 times higher than that in the sputtered electrode due to the larger electrochemically active area.

Although the foregoing argument is directly valid for the catalyst region of the polarization curve, the difference in performance observed at the ohmic and mass

20   transport regions of the curve is only indirectly related to the reduced electrocatalytic active area. Factors which would directly relate to the difference in performance at the ohmic and mass transport regions of the curve would be, e.g., reduced hydration of

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membrane (due to lower current densities) or flooding. These factors, nevertheless, are directly related to current density, which is directly related to the extent of electrocatalytic area.

FE-SEM Analysis: In order to characterize the microstructure of the vacuum

5   catalyzed electrodes, field-emission SEM was performed. FE-SEM micrographs for the uncatalyzed ELAT gas diffusion media were compared to FE-SEM micrographs for the Pt EB-PVD catalyzed ELAT diffusor and Pt sputtered catalyzed diffusor. Magnifications from x5k up to x50k were used. Pictures with x25k and x50k magnification showed most of the differences in structure.

10   Significant differences on the morphology of the Pt catalyst coating were observed between the EB-PVD and magnetron sputtering coating technologies. On the sputtered sample, the Pt particles were in the form of aggregates (Figs. 23-28), and in some cases the particles appeared to coalesce and form larger "fused" particles with a longitudinal dimension (18c, 18d, Fig. 25) of from about 400 to about 1000 nm. In

15   these "fused" particles (18c, 18d, Fig. 25), the outer surface of individual particles was no longer visible (18, 18a, and 18b in Figs. 26 and 27).

On the EB-PVD catalyzed sample, the Pt particles were in the form of aggregates and in some cases the particles (12, Fig. 17) appeared to coalesce and form patches (14, Fig. 17). But the outer surface of individual Pt particles (12, Fig. 17) was

20   readily recognizable in the coalesced patches as compared to that of the coalesced particles in the Pt sputtered sample (18, 18a, 18b, Figs. 26 and 27). In addition, a

2b

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good amount of rod-like Pt particles 10 (Figs. 14, 15, and 17-22) were observed on

the EB-PVD catalyzed sample. These rod-like particles were not observed in the

sputtered sample.

Persons of ordinary skill in the art will recognize that many modifications may

5   be made to the present invention without departing from the spirit and scope of the

present invention. The embodiments described herein are meant to be illustrative only

and should not be taken as limiting the invention, which is defined in the following

claims.